

# PATENT SPECIFICATION

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## DRAWINGS ATTACHED

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## (54) CUTTING TOOL MATERIALS

(71) We, LABORATOIRE SUISSE DE RECHERCHES HORLOGERES, a Swiss Company of, Rue Breguet 2, Neuchatel, Switzerland, do hereby declare the invention, for which we pray, that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to materials which are suitable as materials from which cutting tools can be made.

Cutting tools tend nowadays to be made from materials having characteristics which are a compromise between abrasion resistance and toughness. Of single materials still used, diamond, which is an extremely abrasion resistant material, is unfortunately very brittle. This material is therefore used only in special cases. On the other hand high speed cutting steels, which have been used to a great extent, are comparatively tough, but have low abrasion resistance.

The ideal compromise material therefore is a tough material having a surface layer of a hard, abrasion resistant substance. From such a material a cutting tool which is both tough and abrasion resistant can be made.

The substance for the abrasion resistant coating layer may be a carbide of one of the transition metals of groups 4 to 6 of the periodic table on alumina. These materials in compact form are extremely brittle. Some of them can however be deposited to form thin layers on suitable substrates, and in this form they can be very ductile. For example a layer of titanium carbide can be applied to steel by thermochemical deposition from the gas phase. A difficulty arises however in attempting to combine in a simple way a tough substrate with a very hard but very thin layer of a hard material, only a few  $\mu\text{m}$  thick. The two materials have very different properties and the combination of substrate and surface layer with the desired characteristics has hitherto not resulted in a satisfactory cutting tool.

According to the present invention, a [Price 25p]

bonded material suitable for use as a cutting tool comprises a substrate, and at least two coating layers chemically deposited on the substrate, the top layer being of a carbide of one of the transition metals of groups 4 to 6 of the periodic table, or of alumina, and the or each intermediate layer having the following characteristics: a) its hardness is between the hardness of the substrate and the hardness of the top layer; b) it is more ductile than the top layer; c) its coefficient of thermal expansion is between that of the substrate and that of the top layer; and d) it is partly diffused in the lower adjacent substance and partly in the upper adjacent substance.

We have found that by interposing between a substrate which is tough but has relatively low abrasion resistance and a chemically deposited surface layer of a carbide of one of the transition metals mentioned above or of alumina, at least one intermediate layer having the particular features mentioned above, then a material suitable for making excellent cutting tools is obtained. The bonded composite material obtained has a wear resistance many times higher than that of the hardest hard metals, and a bending rupture strength which can be higher than 200 kg/mm<sup>2</sup>. The toughness of the material is equal to or better than that of the commercially available sintered hard metals.

According to a further aspect of the present invention a process for manufacturing a bonded material in accordance with the invention comprises chemically depositing the substance forming the intermediate layer on to the substrate by chemical reaction from the gas phase and in such a way that the substrate and the intermediate layer diffuse into each other to form a transition zone between them, and depositing the substance forming the top layer on to the intermediate layer by chemical reaction from the gas phase and in such a way that the top layer and the intermediate layer diffuse into each other to form a transition zone.

Preferably, the top layer is applied at a temperature above the melting point of the

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intermediate layer. The top layer may be formed containing carbides, using as the source of carbon, substituted aliphatic, aromatic or cycloaliphatic or heterocyclic hydrocarbons. Particularly suitable are for example methane and dicyclopentadiene.

Various examples of processes and products in accordance with the invention will now be described.

#### EXAMPLE 1

Square cutting plates of a ledeburitic chromium steel were packed in a powder mixture consisting of an inert ceramic mass, chromium and ammonium chloride, and the whole was heated to 900°C. Chromium chloride was formed in the gas phase and reacted on the surfaces of the steel parts to provide a deposit of chromium, part of which diffused into the surface of the steel and formed, together with the carbon of the steel, a mechanically strong and hard bonding layer 5  $\mu$ m thick containing chromium carbides. The pure chromium layer remaining was between 1 and 2  $\mu$ m thick. After this treatment the plates were immersed in a gas mixture containing, by volume, 96% H<sub>2</sub>, 2% CH<sub>4</sub>, and 2% TiCl<sub>4</sub> at a temperature of 900°C, the pressure being 20 Torr. This resulted in the deposition of a TiC top layer 6  $\mu$ m thick. In this latter stage a transition zone is formed in which a part of the chromium intermediate layer reacts with diffusing carbon to form chromium carbide. The end product is a cutting plate which can be used just as it is, without any further treatment. Cutting plates made in this way were used for finish cutting on a lathe workpieces of brass MS 58 and of 1% carbon

steel. The cutting plates had a useful working life between 5 and 20 times better than the customary plates.

#### EXAMPLE 2

Hard metal cutting plates consisting of the carbides WC, TiC, NbC or VC, with Co as the binder were heated to 1020°C in a gas mixture containing, by volume, 97% H<sub>2</sub>, 2% CH<sub>4</sub>, and 1% CrCl<sub>3</sub>. After the deposition of a chromium and chromium carbide layer between 1 and 2  $\mu$ m thick, there was added to the gas 2% by volume of TiCl<sub>4</sub> and the pressure was brought down to 10 Torr. After 4 hours there had been deposited a 3 to 4  $\mu$ m thick layer of titanium carbide containing a little chromium carbide. This layer is harder than a layer of pure titanium carbide. The process described above can also have the effect of increasing the hardness of the original hard metal surface, in that the cobalt binder reacts with the carbides to produce ternary alloys of the type W<sub>3</sub>Co<sub>3</sub>C.

Tests were made by cutting on a lathe workpieces made of steel No. C 100 W 1. When this material was cut using untreated hard metal cutting plates it was found that after 12 minutes of cutting time the plate had suffered an abrasion loss of 0.2 mm, representing the tolerable limit. On the other hand using a cutting plate prepared as described above, under the same cutting conditions, after 30 minutes of cutting time the abrasion loss was found to be only 0.005 mm.

Similar improvements in quality were obtained using the following combinations of substrate, intermediate layer and top layer;

Example No.	Substrate	Intermediate layer or layers	Top layer
3.	NIMONIC (Registered Trade Mark) (for example 80% Ni + 20% Cr)	Ni <sub>3</sub> Al; NiAl (first) (second)	Al <sub>2</sub> O <sub>3</sub>
4.	STELLITE (Registered Trade Mark) (for example 20% Cr, 15% W, 51% Co, ca. 10% Ni, 1.4% NMn, 1.7% Fe)	Cr—Carbides	ZrC
5.	Cr-Mo-C-Steel with 33% TiC	(Mo; MoC (first) (second))	B <sub>4</sub> C

#### EXAMPLE 6

A cutting plate consisting essentially of Al<sub>2</sub>O<sub>3</sub> with Ni as binder was heated to 900°C in hydrogen. After adding 0.5% by volume CrCl<sub>3</sub> and 0.2% by volume dicyclopentadiene

in gaseous form the total pressure was brought down to 15 Torr. After 30 minutes the temperature was lowered to 850°C and there was added as a further reaction gas 2% by volume of TiCl<sub>4</sub>. After a further 60

minutes the reaction gases were replaced with argon and the sample was allowed to cool to room temperature. It was found that there had been deposited on the cutting plate a layer of chromium carbide 1 to 2  $\mu\text{m}$  thick, and over this there had formed a top layer of titanium carbide 8 to 10  $\mu\text{m}$  thick doped with chromium carbide.

The laminated plate made in this way was used for cutting cast steel and gave a working life 6 to 10 times longer than those obtained with the cutting materials customarily used for cutting cast steel.

The main advantage of the present invention is that it provides a material having great toughness with little abrasion loss, and consequently, cutting tools made from the material have a longer working life. Also, higher cutting speeds are possible, resulting in greater output.

It is also possible to use, to some extent, less costly, tougher and more easily worked substrate materials, which have hitherto not been commonly used as materials for cutting tools because they are insufficiently resistant to abrasion. Among these materials are almost all the hardened steels, various nickel alloys, copper alloys, titanium alloys, cobalt alloys and aluminum alloys, various hard metals, all being too soft for cutting, and ceramic sintered materials containing large fractions of binders.

Cutting tools made from materials in accordance with the invention may have abrasion resistance factors greater than those of the commercially available cutting tools by factors between 2 and 20, while retaining a good degree of toughness. As a consequence, these cutting tools may be used to cut materials which, have hitherto been extremely difficult to cut.

The accompanying drawing shows a graph of hardness as a function of bending rupture strength, for various cutting tool materials. The bending rupture strength of a material is closely related to its toughness. Hardness is closely related to abrasion resistance. In the drawing the shaded region A relates to various known cutting tool materials, that is to say special hard metals 1, cutting tool ceramic 2, sintered hard metals 3 and high speed cutting steels 4. The region B relates to the new laminated cutting tool materials.

#### WHAT WE CLAIM IS:—

1. A bonded material suitable for use as a cutting tool, comprising a substrate, and at least two coating layers chemically deposited on the substrate, the top layer being of a carbide of one of the transition metals of groups 4 to 6 of the periodic table, or of alumina and the or each intermediate layer having the following characteristics: a) its hardness is between the hardness of the substrate and the hardness of the top layer; b)

it is more ductile than the top layer; c) its coefficient of thermal expansion is between that of the substrate and that of the top layer; and, d) it is partly diffused in the lower adjacent substance and partly in the upper adjacent substance.

2. A material according to claim 1, in which the substrate is ledeburitic chromium steel, there is an intermediate layer of chromium, and the top layer is titanium carbide, the transition zones between the substrate and the intermediate layer, and between the intermediate layer and the top layer, containing chromium carbide.

3. A material according to claim 1, in which the substrate is tungsten carbide, titanium carbide, niobium carbide or vanadium carbide with a cobalt binder, there is an intermediate layer of chromium and chromium carbide, and the top layer is titanium carbide, the transition zones between the substrate and the intermediate layer, and between the intermediate layer and the top layer, containing chromium carbide.

4. A material according to claim 1, in which the substrate is an alloy containing 80% Ni and 20% Cr, there is a first intermediate layer of  $\text{Ni}_3\text{Al}$ , a second intermediate layer of  $\text{NiAl}$ , and the top layer is  $\text{Al}_2\text{O}_3$ .

5. A material according to claim 1, in which the substrate comprises 20% Cr, 15% W, 51% Co, 10% Ni, 1.4% Mn, and 1.7% Fe, there is an intermediate layer of chromium carbides and the top layer is zirconium carbide.

6. A material according to claim 1, in which the substrate is a Cr—Mo—C steel containing 33%  $\text{TiC}$ , there is a first intermediate layer of molybdenum and a second intermediate layer of molybdenum carbide, and the top layer is the boron carbide  $\text{B}_4\text{C}$ .

7. A process for manufacturing a bonded material according to claim 1, in which the substance forming the intermediate layer is chemically deposited on to the substrate by chemical reaction from the gas phase and in such a way that the substrate and the intermediate layer diffuse into each other to form a transition zone between them, and the substance forming the top layer is deposited on to the intermediate layer by chemical reaction from the gas phase and in such a way that the top layer and the intermediate layer diffuse into each other to form a transition zone.

8. A process according to claim 7, in which the top layer is formed containing carbides, the source of the carbon being substituted aliphatic, aromatic, cycloaliphatic or heterocyclic hydrocarbons.

9. A process according to claim 8, in which the source of carbon is methane.

10. A process according to claim 8, in which the source of carbon is dicyclopentadiene.

11. A process according to claim 7, in which the substrate is a cutting plate made of a ledeburitic chromium steel and is packed in a powder mixture consisting of an inert ceramic mass, chromium and ammonium chloride, the whole is heated to 900°C to form chromium chloride in the gas phase, the chromium chloride being reacted on the surface of the plate to form a chromium intermediate layer part of which is diffused into the surface of the plate and forms with the carbon of the steel plate chromium carbide, and then a top layer of titanium carbide is deposited on to the surface of the intermediate layer by reaction in the gas phase between the intermediate layer and a mixture containing by volume 96% hydrogen, 2% methane and 2%  $\text{TiCl}_4$ , at 900°C and a pressure of 20 Torr, the chromium and the titanium carbide partly diffusing into each other with the formation of chromium carbide.

12. A process according to claim 7, in which the substrate consists of tungsten carbide, titanium carbide, niobium carbide or vanadium carbide, with a cobalt binder, and is given a coating of chromium and chromium carbide as the intermediate layer by reaction at 1020°C with a gas mixture consisting of 97% hydrogen, 2% methane and 1%  $\text{CrCl}_3$ , by volume, the chromium partly diffusing into the surface of the substrate and forming chromium carbide, and then a top layer of titanium carbide is deposited on to the intermediate layer by reaction at 1020°C and a

pressure of 10 Torr between the intermediate layer and the gas mixture after the addition to it of 2%  $\text{TiCl}_4$  by volume, the chromium and the titanium carbide partly diffusing into each other to form chromium carbide.

13. A process according to claim 11, in which the substrate is a cutting plate consisting substantially of  $\text{Al}_2\text{O}_3$  with nickel as binder, and is heated to 900°C in hydrogen, 0.5%  $\text{CrCl}_3$  and 0.2% dicyclopentadiene by volume is added to the hydrogen and the pressure is reduced to 15 Torr so that chromium carbide is deposited as the intermediate layer, and after 30 minutes the temperature is reduced to 850°C and 2% by volume gaseous  $\text{TiCl}_4$  is added to the hydrogen with the result that after a further 60 minutes a top layer of titanium carbide is formed doped with chromium carbide.

14. A process according to claim 7, substantially as described in any one of the examples 1, 2 and 6 described herein.

15. A material produced by a process according to claim 14.

16. A material according to claim 1, substantially as described in any one of examples 3 to 5.

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